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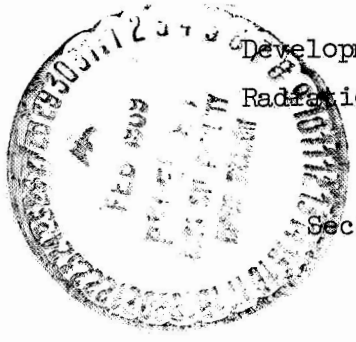

Development of Lithium Diffused Radiation Resistant Solar Cells

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ABSTRACT

During this quarter, various aspects of the lithium cell fabrication process have been investigated. These include application of the lithium by evaporation rather than by the paint-on technique; comparison of the use of an SiO layer to the use of the blue layer obtained in boron diffusion for antireflection layers; and preliminary investigation of sintering lithium cells.

The third and fourth lots of lithium cells have been fabricated and delivered to JPL. Yield analyses of these cells have been made and comparison was also made to the first two lots.

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1.0 INTRODUCTION

The goal of this contract is to investigate process parameters which may influence lithium solar cell performance. This includes such areas of study as the starting material, the lithium and boron diffusions, and any other processes which are included or might be added to the lithium cell fabrication process.

With respect to starting material, the type of crystal is of particular interest. The room temperature or low temperature recovery of lithium cells fabricated from crucible grown silicon has been a recent enough discovery that very little information has been obtained on these cells. The extremely good characteristics of these cells make them an important area for study, particularly in the early part of the contract period since their recovery after radiation is slower than the recovery of lithium cells fabricated from float zone silicon.

In general, lithium cells have lower efficiencies than standard 10 ohm cm N/P cells. Even so, the lithium cells compare favorably after radiation to the N/P cells. It is quite probable that if the efficiency could be increased, lithium cells would be an improvement over the N/P cell in a radiation environment. Since some high efficiency lithium cells have been obtained, the problem is one of improving uniformity and yields by improving processes and techniques. The main areas of study for improving cell efficiency will be the lithium and boron diffusions.

A major part of this program will be the fabrication of 600 experimental lithium solar cells for radiation testing and analysis by JPL. These same cells will be part of the groups of cells used for statistical analyses of the short circuit current and maximum power during the contract period.

2.0 TECHNICAL DISCUSSION

2.1 PROCESS STUDIES

The variations in the electrical output of lithium cells is of major concern at this time. In the past, studies of the lithium application process have resulted in refinements to the extent that huge pits in the silicon slice have been eliminated and due to this improvement cell breakage was reduced considerably. And while this improvement may have eliminated the low output cells which had low outputs because they were strained and about to break, there was still a problem of large output variations.

These variations may be inherent in the lithium paint-on technique and for this reason evaporation of the lithium has been studied. Past work on applying the lithium layer by evaporation has shown that oxidation of lithium while opening the vacuum system and transferring the cells to the diffusion furnace was a problem. For this reason the emphasis has been on covering the evaporated lithium layer with some other material in order to eliminate or reduce the lithium oxidation. Aluminum was the first material investigated for coating the lithium. On the first Li-Aℓ evaporation rapid oxidation occurred instantaneously when air was let into the vacuum system and it made the Li-Aℓ layer peel and flake off. By leaking the air in more slowly some evaporations were obtained in which the Li-Aℓ layer did not peel and flake off. The cells were diffused 90 minutes at 425°C and after diffusion V/I's were measured using the four point resistivity probe. They varied more than V/I's measured on cells where lithium was painted on; for the diffusion parameters used the V/I's normally vary from .22 to .28, but when the evaporation was used V/I's ranged from .22 to 1.21. V/I's indicate that uniform doping is obtained using the paint-on technique and yet large variations in the electrical characteristics occur. The evaporation technique must at least give uniform doping or there is no hope for

uniformity of electrical characteristics. Since the V/I range was large and it was difficult to remove the cells from the vacuum system without getting rapid oxidation, aluminum was eliminated as a suitable coating material. Silver was also used as the protection metal in several experiments.

The first evaporation was set up such that the cells which got the thinner layer of lithium got the thicker layer of silver and the cells with the thicker layer of lithium got the thinner layer of silver. The result of this situation was peeling on the cells with the thicker lithium and thinner silver layers. The amount of lithium was then decreased and silver increased. The resulting layer did not peel so the cells were diffused. Afterward, V/I's were measured, but they indicated that no significant lithium diffusion occurred. This could be caused by two things: either the lithium oxidized before the cells were put into the diffusion furnace or the lithium did not alloy to the cell surface and therefore did not diffuse. Since the Li-Ag layer reacted when a couple of cells were dropped into water after the evaporation, this indicated the presence of lithium metal so the lithium should have been present for diffusion. Therefore, for some reason the lithium did not alloy. This problem will be investigated further during the next quarter.

The lithium diffusion is one of the major areas under investigation; however, other processes in lithium cell fabrication are being looked at. In the standard fabrication procedure, the blue layer obtained during boron diffusion is removed by HF before contact application, leaving a grey to grey-blue surface which is later covered with a SiO antireflection coating. An experiment was performed to compare the short circuit current of cells with the standard SiO antireflection coating to the short circuit current of cells which did not have the blue layer etched off. I-V curves of both groups were measured in a 100 mW/cm^2 tungsten light source and in the Spectrosun solar simulator at an intensity of 140 mW/cm^2. Table I shows the average

short circuit current values obtained from the two groups of cells; Group A had the SiO coating and Group B had the blue layer from boron diffusion. Before SiO coating the average I_{sc} of the cells in Group A was slightly lower than the average I_{sc} of the cells in Group B - 52.1 versus 52.5. However, when Group A cells were SiO coated the average I_{sc} in a 100 mW/cm^2 tungsten light source was 58.7 mA, which was more than 10% higher than the I_{sc} of Group B cells. When Group A and B cells were measured in the solar simulator the difference between the two group's average I_{sc} decreased to less than 10%; however, on an absolute scale, the difference between the short circuit currents of Groups A and B measured in the simulator and in tungsten was nearly the same -- 6.0 mA difference in the simulator versus 6.4 mA in tungsten. After measuring the I_{sc} of Group B cells in the simulator and finding it to be lower than the I_{sc} of Group A cells, an SiO layer was evaporated over the blue layer of Group B cells. This only increased the average I_{sc} 1.1 mA, indicating that the blue layer-SiO layer is optically inferior to the antireflective layer obtained by SiO coating a cell without the blue layer.

In standard lithium cell processing, sintering the Ti-Ag contacts has not been utilized since a good ohmic contact is obtained without sintering. From time to time the series resistance is higher and for this reason investigation of the effect of sintering on the P/N lithium cell has been started. I-V curves taken of a group of lithium cells before and after sintering showed a significant increase in short circuit current (6%) and a drastic increase in series resistance; Figure 1 shows the characteristics of a typical cell. The cells were sintered a second time and this resulted in a slight short circuit current increase and a large decrease in the series resistance. At this point the maximum power which had started out at 24.3 mW before sintering and dropped to 21.5 mW after the first sintering had increased to 24.7 mW which was higher than the initial power output. A third

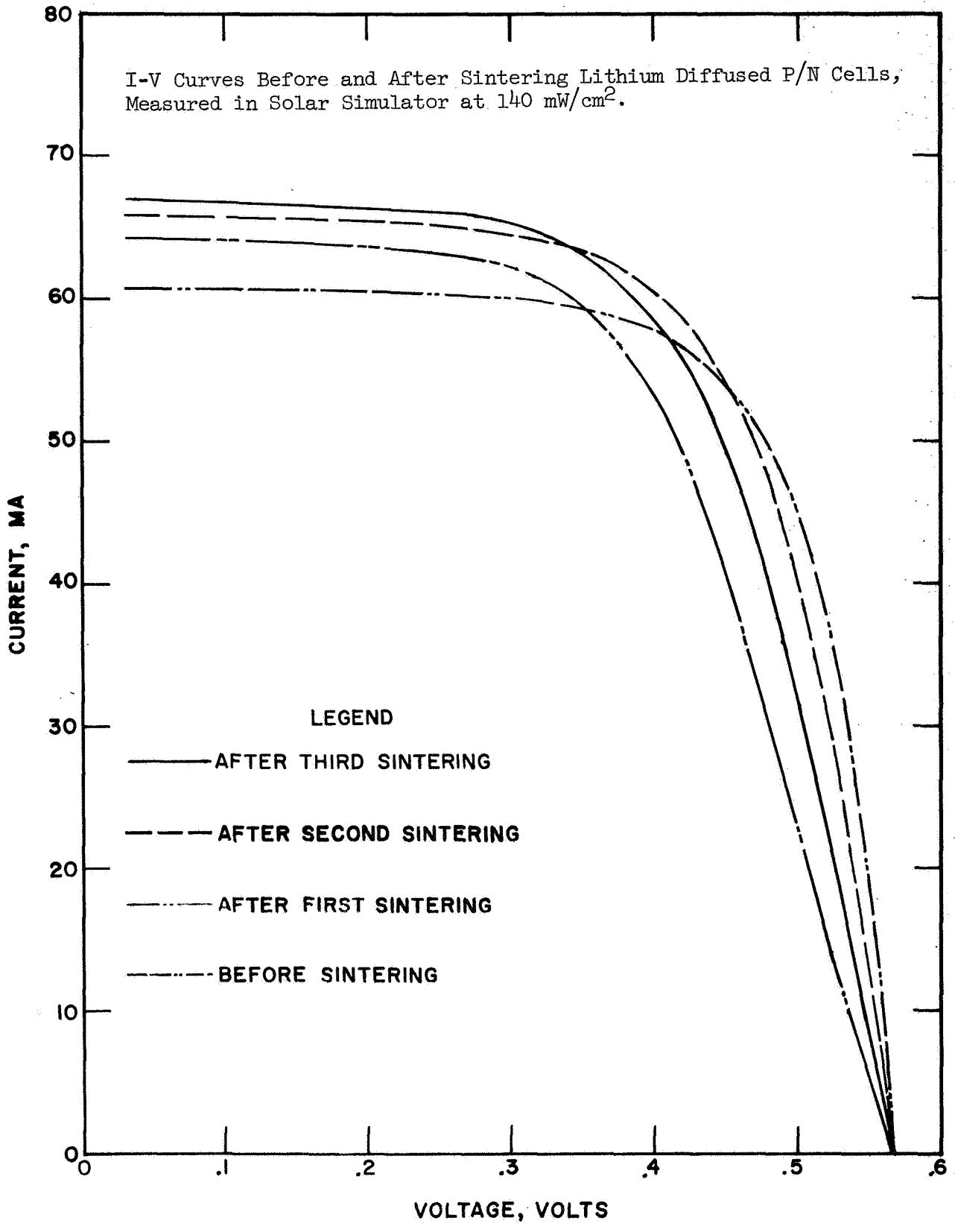
I-V Curves Before and After Sintering Lithium Diffused P/N Cells, Measured in Solar Simulator at 140 mW/cm2.
CURRENT, MA
VOLTAGE, VOLTS
0
10
20
30
40
50
60
70
80
.1
.2
.3
.4
.5
.6
LEGEND
AFTER THIRD SINTERING
AFTER SECOND SINTERING
AFTER FIRST SINTERING
BEFORE SINTERING

Figure 1.

sintering resulted in another slight short circuit current increase, however, the series resistance again increased. The short circuit current increases with each sintering step. The initial increase of 3.6 mA was $\approx$ twice that of each successive increase and may have been due to both lithium movement and a gettering action. This seems to be supported by the fact that short circuit current increases are observed with sintering of P/N cells without lithium. These multiple sinterings of lithium cells have indicated that there may be a heat treatment which results in a definite improvement in the cell output without damaging any other characteristics. The problem must be studied further to determine the optimum conditions. This study should include investigation of the effect of the heat treatment(s) on the lithium distribution and the radiation resistance.

TABLE I

Average I_{sc} of P/N Cells

SiO Layer versus Blue Layer from Boron Diffusion

Light source	Type and/or Condition of Antireflection Layer	I_{sc}, mA
Group A		
100 mW/cm^2 tungsten	before SiO coating	52.1
100 mW/cm^2 tungsten	after SiO coating	58.7
140 mW/cm^2 solar simulator	after SiO coating	71.1
Group B		
100 mW/cm^2 tungsten	blue layer from boron dif.	52.5
140 mW/cm^2 solar simulator	blue layer from boron dif.	65.1
140 mW/cm^2 solar simulator	blue layer and SiO	66.2

2.2 CELLS FOR SHIPMENT

The third and fourth shipments consisted of 20 ohm cm Mon-x and 100 ohm cm float zone lithium cells, respectively; a 90 minute diffusion with 60 minutes redistribution at 425°C was used for both shipments. For each shipment the group of cells fabricated exceeded the 60 cells delivered and the total number of cells in each group was used for statistical analysis of the distribution. As seen in Figure 2, the maximum power distributions for the two shipments were very similar. Of the 117 Mon-x cells fabricated 5% were above 26.6 mW, 95% were above 21.1 and the mean maximum power was 23.6 mW; at these same points the group of seventy 100 ohm cm float zone cells had maximum powers of 26.0, 21.6, and 23.3 mW. With respect to the short circuit current (see Figure 3), the cells in both groups showed approximately the same distribution with 5% of the cells in both groups having short circuit currents of 63.1 mA or above. Below 60 mA the distribution of Mon-x cells was lower with 95% of the cells having short circuit currents of 53.6 mA or above, while for the 100 ohm cm float zone cells this 95% point was at 54.7 mA. The mean for the Mon-x cells was 57.2 mA, for the 100 ohm cm float zone cells, 58.0 mA. As seen in Figures 1 and 2, the electrical characteristics of Mon-x and float zone lithium cells were very similar. Figure 4 shows the maximum power distribution of float zone and Mon-x lithium cells and compares them to the maximum power distributions of crucible grown lithium cells. Even in the lowest distribution of crucible grown lithium cells, 80% of the cells have outputs 1-3 mW higher than the float zone and Mon-x cells. The highest distribution curve shown was obtained from 20 ohm cm Czochralski grown lithium cells fabricated for the second shipment; this distribution is about 5 mW higher than the Mon-x and float zone cells. This difference in output between crucible grown and float zone or Mon-x lithium cells is caused by higher short circuit currents and open circuit voltages and less series resistance in the crucible grown lithium cells.

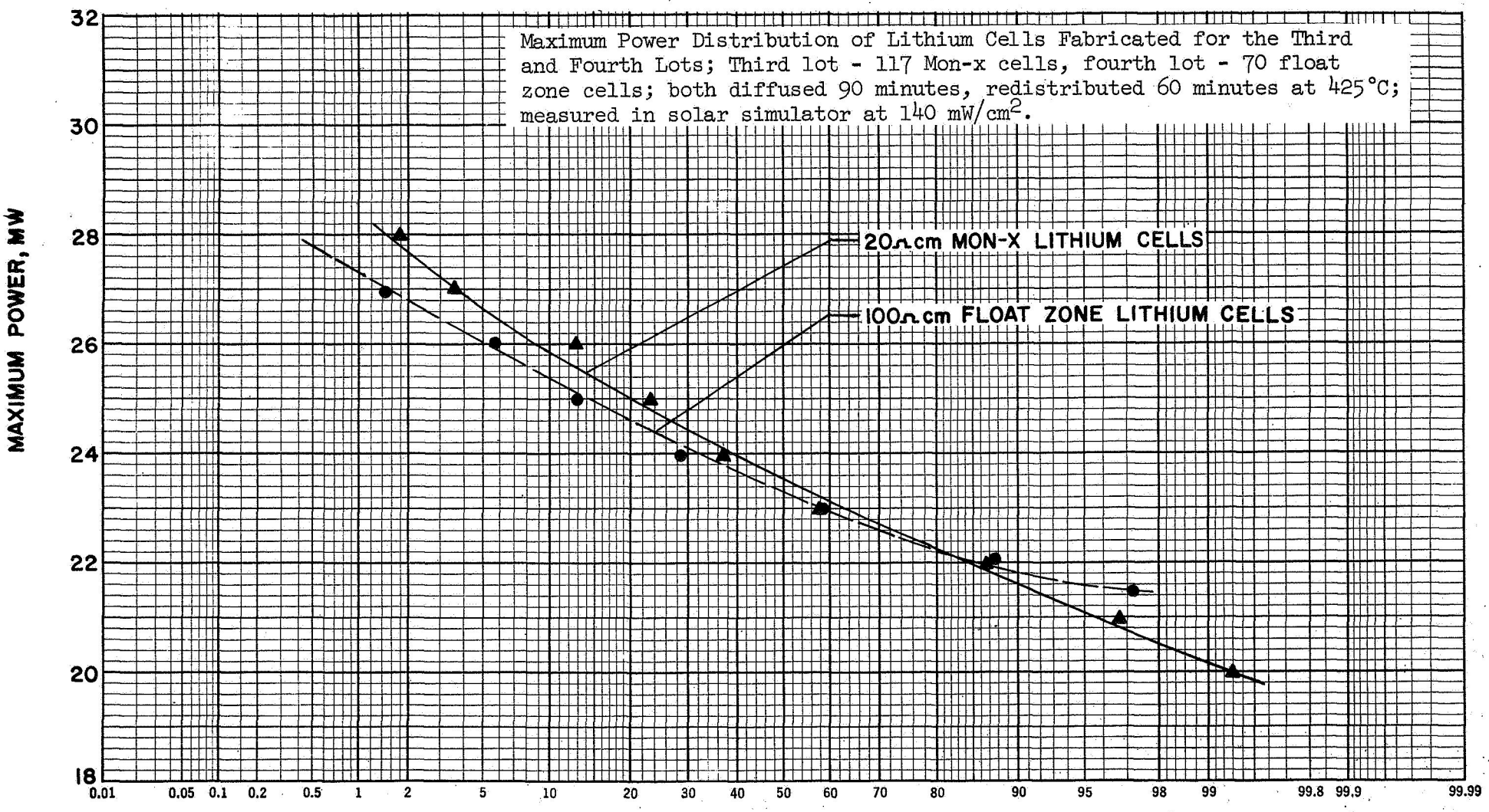
Maximum Power Distribution of Lithium Cells Fabricated for the Third and Fourth Lots; Third lot - 117 Mon-x cells, fourth lot - 70 float zone cells; both diffused 90 minutes, redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm2.
20Ω cm MON-X LITHIUM CELLS
100Ω cm FLOAT ZONE LITHIUM CELLS
MAXIMUM POWER, MW
32
30
28
26
24
22
20
18
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
% OF CELLS GREATER THAN A GIVEN MAXIMUM POWER

Figure 2.

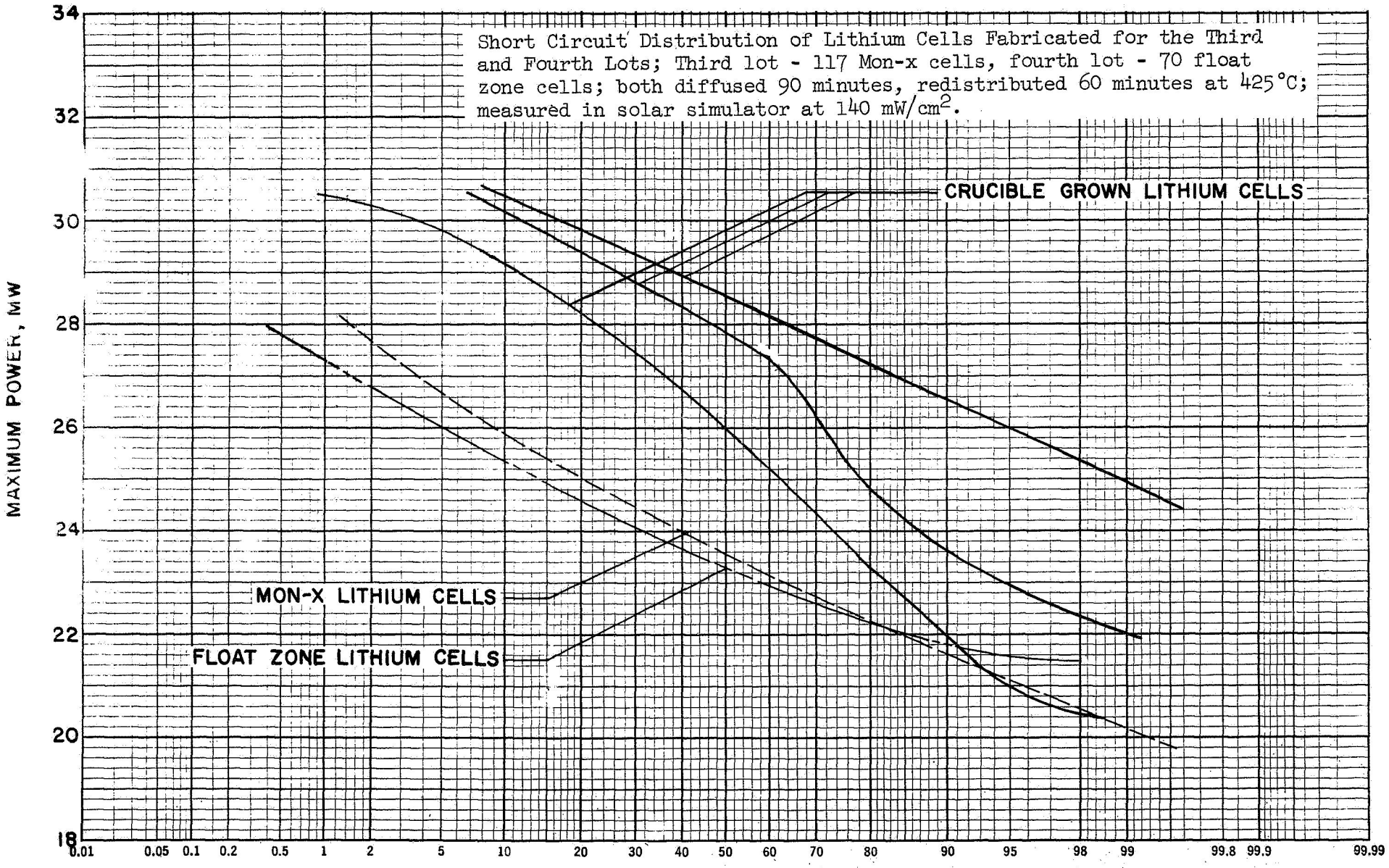
Short Circuit Distribution of Lithium Cells Fabricated for the Third and Fourth Lots; Third lot - 117 Mon-x cells, fourth lot - 70 float zone cells; both diffused 90 minutes, redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm2.
CRUCIBLE GROWN LITHIUM CELLS
MON-X LITHIUM CELLS
FLOAT ZONE LITHIUM CELLS
MAXIMUM POWER, MW
34
32
30
28
26
24
22
20
18
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
% OF CELLS GREATER THAN A GIVEN MAXIMUM POWER

Figure 3.

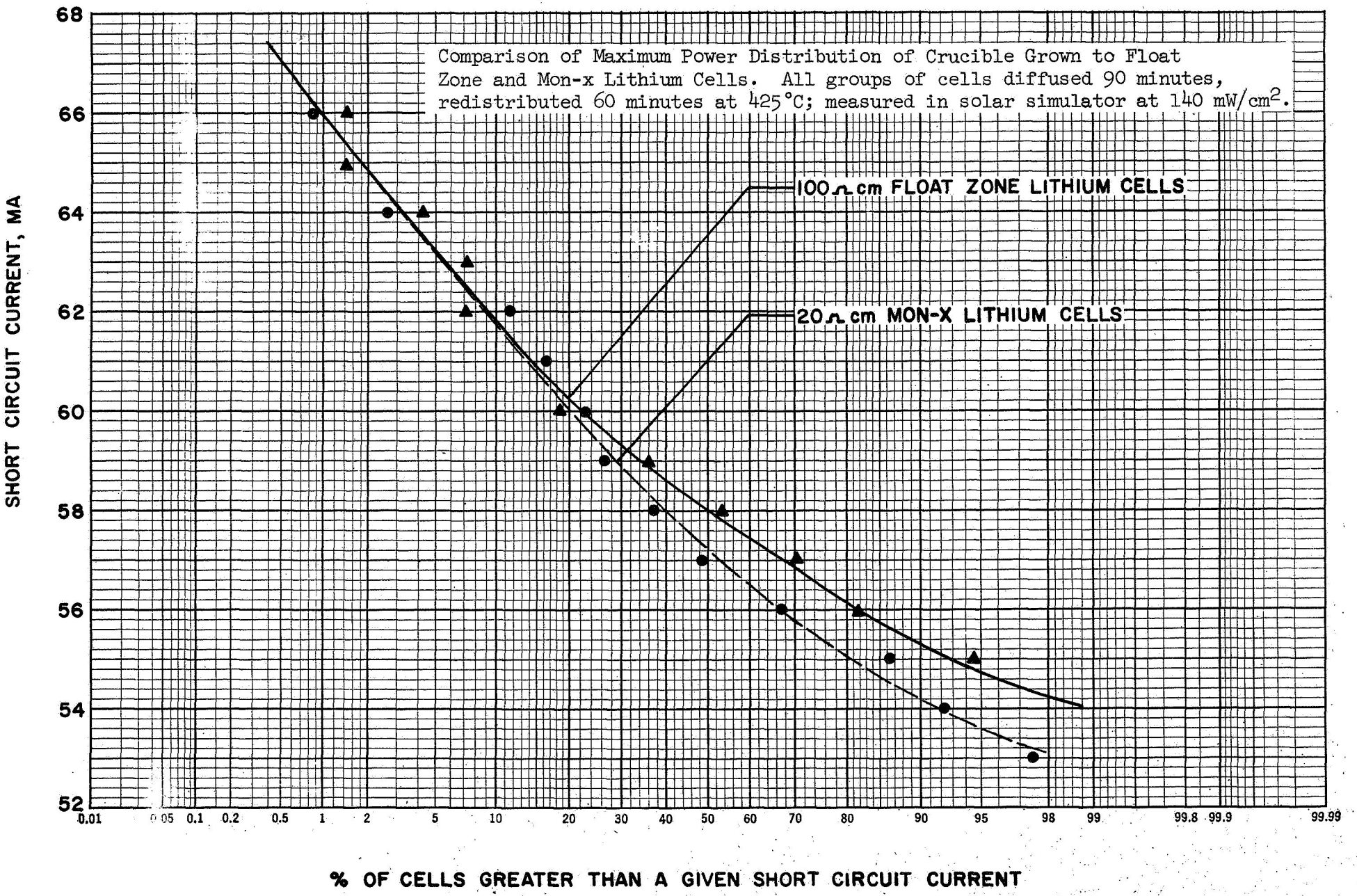
Comparison of Maximum Power Distribution of Crucible Grown to Float Zone and Mon-x Lithium Cells. All groups of cells diffused 90 minutes, redistributed 60 minutes at 425°C; measured in solar simulator at 140 mW/cm2.
100Ω cm FLOAT ZONE LITHIUM CELLS
20Ω cm MON-X LITHIUM CELLS
SHORT CIRCUIT CURRENT, MA
68
66
64
62
60
58
56
54
52
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
% OF CELLS GREATER THAN A GIVEN SHORT CIRCUIT CURRENT

Figure 4

For some reason, the same lithium diffusion parameters used on the three types of silicon do not give the same electrical characteristics. It does not seem to be dependent upon the number of dislocations since the Mon-x silicon resembles crucible grown silicon with respect to dislocations, but the Mon-x lithium cells are electrically comparable to float zone not crucible grown lithium cells. The factor which distinguishes both float zone and Mon-x from crucible grown silicon is the oxygen concentration. The presence of more oxygen seems to make it possible to obtain higher open circuit voltages and to dope with lithium to higher levels without damaging the lifetime and decreasing the short circuit current.

3.0 CONCLUSIONS

At this time the application of lithium by evaporation is not as repeatable nor does it yield results as uniform as those obtained with the paint-on technique.

The SiO layer is superior to the blue layer obtained in boron diffusion or the blue layer-SiO combination as an antireflection layer.

The preliminary investigation on sintering lithium cells has indicated that sintering may improve lithium cell efficiencies. However, this should be thoroughly checked before sintering is utilized as a standard process in lithium cell fabrication. This investigation should also include radiation analysis of sintered and unsintered cells since any heat treatment is going to affect the lithium distribution and possibly the radiation recovery characteristics. The average output of cells fabricated for the third lot was 23.6 mW or an AMO efficiency of 8.7%, and for the fourth lot, 23.3 mW or an AMO efficiency of 8.6%. The average outputs of the first two lots which were fabricated with crucible grown silicon were considerably higher than these obtained from the third and fourth lots.

For some time now it has been observed that higher efficiency lithium cells could be obtained with crucible grown silicon than with float zone silicon. The yield analyses performed in the past two quarters have given statistical support to this claim. This should indicate clearly that there will be no single optimum lithium cell design; rather, the design will depend upon level of radiation to be seen, amount of recovery time available, and cell output needed.

4.0 RECOMMENDATIONS

More work should be done on lithium evaporations since if this can be done repeatedly, it should have a beneficial effect upon the cell uniformity. Even if there were no uniformity improvement, but only a maintaining of present uniformity, evaporation would be less tedious and time consuming than the paint-on technique.

Investigation of the effect of sintering upon lithium cells should continue. If sintering continues to give good results, lots of sintered and unsintered cells with the same diffusion parameters should be subjected to radiation and analyzed for any differences which might occur as a result of the heat treatment.

5.0 NEW TECHNOLOGY

None